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Dye-sensitization on the Photocurrent at Zinc Oxide Electrode in Aqueous Electrolyte Solution

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The dye-sensitized photocurrents generated from the electrochemical systems <zinc oxide|aq solution|platinum> have been studied. The action spectra for the photocurrent, its dependence on the concentration of the dye solution and other experimental results have revealed that the photocurrent is caused by the dye adsorbed on the electrode, not from that dissolved in the liquid phase. From the analysis of the decay of the photocurrent with the time of illumination, the quantum yield for the electron injection from the excited dye has been determined. Rose Bengal showed the quantum yield of 22%. The influence of halide ions on the photocurrent has also been studied.

"Wet-type" photocells, consisting of a semiconductor electrode, an aqueous solution, and a metal counter electrode, are attracting growing attention as a device to convert light energy into electrical or chemical energy.[1-4] The photovoltaic effect in such cells arises essentially from generation of electrons and holes in the illuminated semiconductor electrode and their efficient separation by the built-in electric field inside the space charge layer of the semiconductor. One of the characteristics of the "wet" cells is that the photocurrent is accompanied by redox reactions of the solute or the solvent in the electrolyte solution.

When the electrolyte solution contains a dye, a photocurrent often flows by the excitation of the dye with photon energy less than the band gap of the semiconductor. In this case, the current is called the dye-sensitized photocurrent, on which many reports have been made.[5-9]

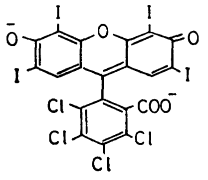
We have succeeded in constructing a dye-sensitized semiconductor photo-cell having an energy conversion efficiency of 1.5% under monochromatic illumination.[10] In order to increase the energy conversion efficiency further, it will be necessary to increase both the quantity of light absorbed by the dye and the quantum yield of electron injection from the excited dye. For this purpose, it is essential to deepen our understanding on the mechanism of electron transfer in such systems. In this paper, we describe some of our results on such problems.

Experimental

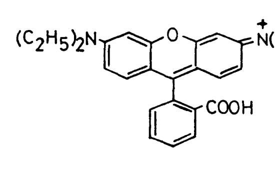
Zinc oxide sinter disks were used as the electrodes. They were prepared by moulding zinc oxide powder by compression and heating at 1300 °C in the air for 1 h. It was found that the adsorptive activity of the zinc oxide sinter for the dye depends on the source of the zinc oxide powder. In the following experiments, we made the sinter out of zinc oxide powder obtained from Kanto Chemical Co. without any purification or pre-treatment. The sinter had low adsorptive activity but gave a reproducible photocurrent. One of the surfaces of the zinc oxide disk was coated with indium by employing the evaporation method so as to make an ohmic contact, and a copper wire was attached with silver paste. The structure of the electrode was mostly the same as that described previously.[9,10] Before each measurement, the electrode was polished with silicon carbide abrasive, etched with hydrochloric acid or nitric acid, washed with water, and dried.

The potential of the semiconductor electrode *versus* the reference electrode (SCE) was controlled by use of a Hokutodenko HA-101 potentiostat and the current was measured with a Yokogawa-Hewlett-Packard 4304B electrometer. A 500 W xenon lamp of Ushio Electric Inc. was used as the light source. The light was monochromatized by use of a Japan Jarrel-Ash, 0.25 m Ebert type monochromator. The light intensity was measured with an Eppley, bismuth-silver type thermopile. A Shimadzu MPS-50L Spectrometer was used for the measurements of absorption spectra.

All the solutions used contained 0.2 M (mol·dm^{-3}) Na_2SO_4 or KNO_3 as the supporting electrolyte. Oxygen was removed by bubbling high purity nitrogen gas through the solutions before measurement. All chemicals were of reagent grade and used without further purification. The structual formulas of the dyes used are given below:



Rose Bengal.



Rhodamine B.

Results

Figure 1 shows the dye-sensitized photocurrent-potential curves for the case of Rose Bengal. The anodic current was negligible in the dark, while it rose up under illumination in the wavelength range of the absorption band of Rose Bengal. When the solution contained no dye, the photocurrent was less than 0.03

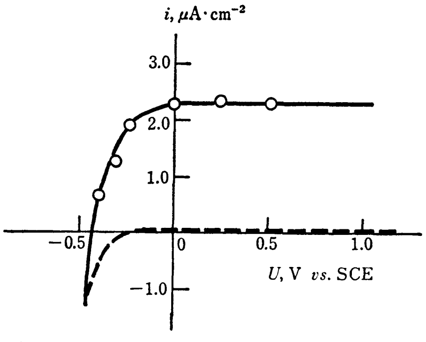


Fig. 1. Current-potential curves in the presence of 6.5×10^{-7} M Rose Bengal and 0.2 M Na_2SO_4, ----dark current, ——under illumination (λ 562 nm).

$\mu A \cdot cm^{-2}$ under illumination at the same wavelength and at the electrode potential of 0.35 V. Since the photocurrent decayed during the course of illumination, the photocurrent curve was plotted by using the value obtained immediately after the light had been turned on. The photocurrent appeared at the electrode potential more positive than −0.5 V *vs.* SCE, which nearly agreed with the flat band potential of the zinc oxide electrode reported by Lohmann,[11] and became constant at the potential more positive than 0.0 V. Therefore, most of the experiments were made at 0.35 V.

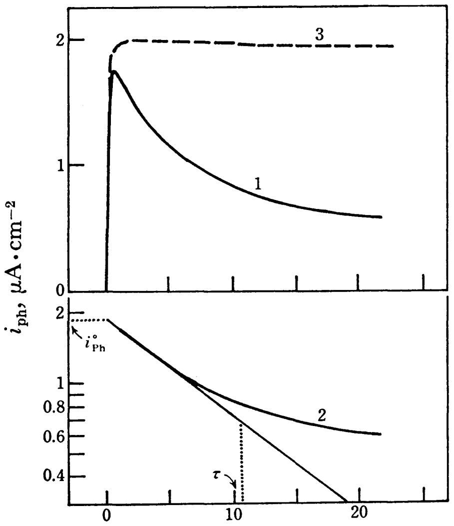


Fig. 2. The change of the photocurrent *vs.* time. Curve 1, for the solution of 6.7×10^{-7} M Rose Bengal and 0.2 M KNO_3. Curve 2, the logarithmic plot of the same result. Curve 3, for the case where 0.1 M KI is added.

The photocurrent decayed rather quickly with time as shown in Fig. 2. The photocurrent was not restored to the initial value, if the electrode was kept in the dye solution for a few minutes. The photocurrent fell down to zero when the light was turned off, and no overshoot to the cathodic side was observed. The decay of the photocurrent was suppressed or stopped by adding a reducing agent, *e.g.*, potassium iodide, as shown by curve 3. The logarithm of the photocurrent gave a straight line for the first several seconds as shown by curve 2, from which we can obtain the initial value of the photocurrent, i^0_{ph}, and the decay time constant, τ, namely the period of illumination for which the current decays to 1/e.

The surface of the zinc oxide electrode faintly colored pink, if it was dipped into the Rose Bengal solution. After prolonged illumination in the same solution at closed circuit, the color changed to brown-red. The color was not removed by washing with water. On the other hand, no color change occurred when the elctrode was illuminated at open circuit or at closed circuit in the presence of a reducing agent.

Figure 3 shows the photocurrent action spectrum obtained for a solution containing a sufficient amount of potassium iodide. Almost the same action spectrum was obtained for a solution without any reducing agent by scanning rapidly under weak illumination. The peak of the action spectrum for the photocurrent shifted by 13 nm toward the longer wavelength from that of the absorption spectrum of the dye solution, and nearly coincided with that of the reflection spectrum of the dye adsorbed on zinc oxide powder.

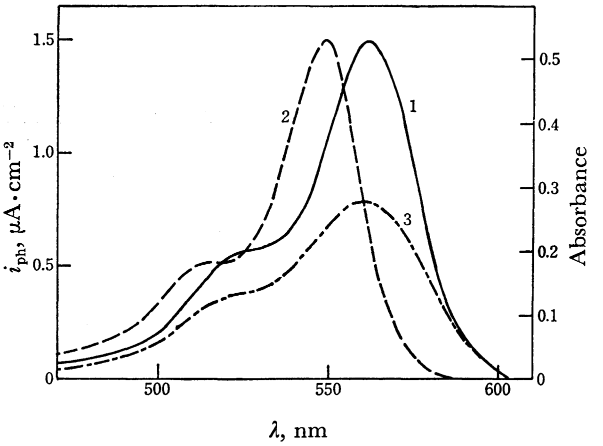


Fig. 3. (1) The action spectrum for the photocurrent for the solution of 5.3×10^{-7} M Rose Bengal and 0.1 M KI at the electrode potential: 0.35 V *vs.* SCE. (2) Absorption spectrum of the same solution, measured with a 10 cm cell. (3) Diffuse reflectance spectrum of the dye adsorbed on zinc oxide powder. The dye was adsorbed in the aqueous solution of 1.4×10^{-5} M Rose Bengal.

The initial value of the photocurrent increased proportionally with the illumination intensity, while the decay time constant was inversely proportional to it (Fig. 4). The value of i^0_{ph} and τ scarcely changed over the electrode potential range 0.0—1.0 V. Figure 5 shows the change of i^0_{ph} and that of τ with the concentration of Rose Bengal in the solution. The i^0_{ph} value increased with the concentration of the dye and ap-

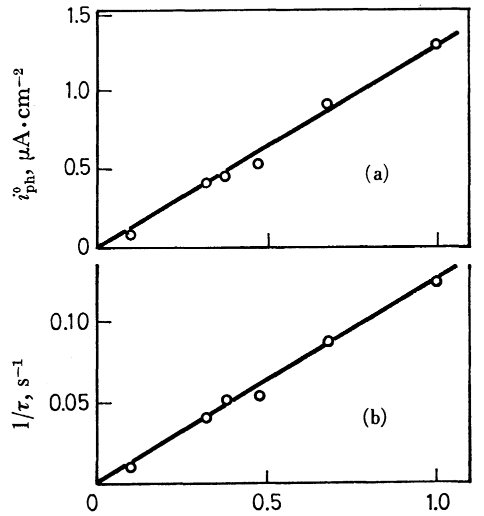


Fig. 4. The change of the initial value of the photocurrent (a), and the decay time constant of the photocurrent (b) with the light intensity: Rose Bengal, 6.5×10^{-7} M; Na_2SO_4, 0.2 M; electrode potential, 0.2 V *vs.* SCE.

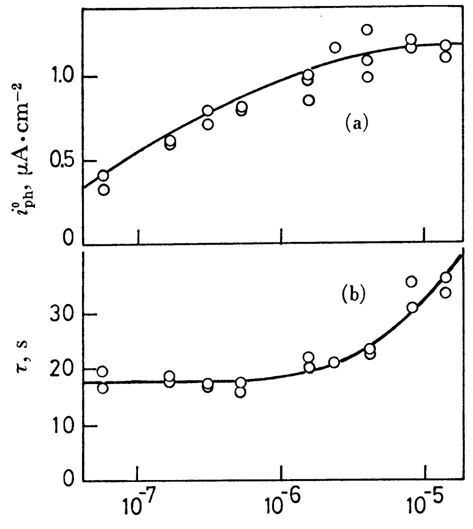


Fig. 5. The initial value of the photocurrent (a) and the decay time constant of the photocurrent (b) *versus* the concentration of Rose Bengal: Na_2SO_4, 0.2 M; electrode potential, 0.35 V *vs.* SCE.

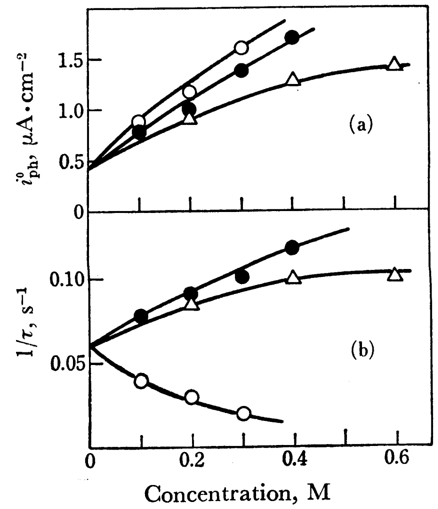


Fig. 6. The initial value of the photocurrent (a) and the decay time constant of the photocurrent (b) *versus* the concentration of the halide ions, Rhodamine B: 1.0×10^{-6} M, Na_2SO_4: 0.2 M, electrode potential: 0.2 V *vs.* SCE; △, chloride ion; ●, bromide ion; ○, iodide ion.

proached a constant. The τ was constant for the concentration of Rose Bengal up to 10^{-6} M, and increased by the concentration above 10^{-6} M.

The photocurrent for Rhodamine B increased by addition of halide ions to the dye solution, while the dependence of the decay time constant of the photocurrent on the concentration of the halide ions was more complicated (Fig. 6a and b).

Discussion

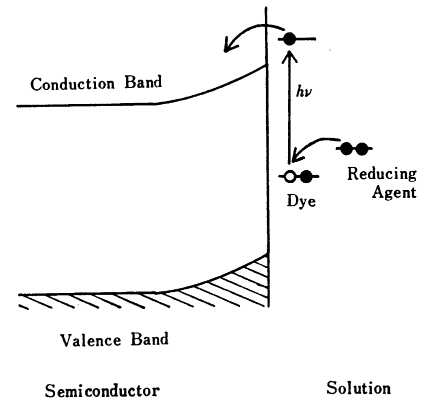


Fig. 7. A model for the electron injection.

The mechanism of the dye-sensitized photocurrent can be explained by the energy diagram such as shown in Fig. 7, for the case of an n-type semiconductor. The electron injection from an excited dye (D^*) into a conduction band is suggested by the fact that only those dyes whose excited energy levels are considerably higher than the conduction band of the semiconductor at the interface can act as effective sensitizers.[12] The electron deficient dye (D^+) may undergo irreversible reaction, causing the color change of the electrode. The total reaction scheme can be represented as follows:

$$D + h\nu \longrightarrow D^*, \tag{1}$$

$$D^* \longrightarrow D^+ + e(\text{electrode}), \tag{2}$$

$$D^+ \longrightarrow \text{reaction product.} \tag{3}$$

It has been tacitly assumed by many authors so far that the dye-sensitized photocurrent is caused by the dye adsorbed on the electrode and not by that dissolved in solution. However, there has been no strong evidence for this. Now, we can pick up the following three facts as such evidence from our experimental results.

1. The shift of the action spectrum for the photocurrent from the absorption spectrum of the solution, as shown in Fig. 3, indicates that the photocurrent is caused mainly by the dye adsorbed on the electrode.
2. From the initial value of the photocurrent shown in Fig. 2, the apparent quantum yield of the photocurrent (η), defined as the number of electrons transferred divided by the number of incident photons, can be calculated to be 1.8%, which means that at least 1.8% of the photons are absorbed by the dye. If the photocurrent is assumed to be caused only by the dye in the bulk of the solution, 3 mm of the light path length in the solution is required to make the absorption factor of the light 1.8% at λ=562 nm. However, the same photocurrent was observed with a light path length of 0.2 mm or shorter. This result indecates that the contribution of the dye in the solution is small or negligible.
3. As shown in Fig. 5, the photocurrent indicates the tendency of saturation at a relatively low concentration of the dye, *i.e.*, 5×10^{-6} M. It would be difficult to explain this by attributing the photocurrent to the dissolved dye. From our preliminary experiments, the adsorption isotherm of the dye adsorbed on the electrode surface has been found to be saturated at about the same low dye concentration as above.

The Decay Curve of the Photocurrent and the Quantum Yield of Electron Injection from the Excited Dye. The photocurrent of some semiconductor-aqueous solution photocell decays with time owing to the deposition of opaque substance on the surface of the electrode, produced by the reaction with the holes generated. The photocurrent in the case of zinc oxide electrode does not decay, because in this case the products, zinc ion and oxygen, do not accumulate on the surface.[13)]

In the case of the dye-sensitized photocurrent for zinc oxide, the photon energy is less than the band gap, and so it is clear that the decay is not caused by the reaction of the electrode itself, since no free hole exists in the electrode. The decay of the photocurrent should then be attributable either to the decrease of the number of the unoxidized dye molecules (or ions) adsorbed on the electrode or to an accumulation of the deteriorated dye (Reactions 1—3).

The influence of the dye (D_{soln}) or the reducing agent (R_{soln}) in solution on the decay of the photocurrent, as shown in Figs. 2 and 5, is explained by the following dye regeneration processes:

$$D^+ + D_{soln} \longrightarrow D + D^+_{soln}, \tag{4}$$

$$D^+ + R_{soln} \longrightarrow D + R^+_{soln}. \tag{5}$$

Process 4 can be achieved either by the electron transfer or by the exchange of D^+ and D_{soln}. The decay of the photocurrent is suppressed if the reaction velocities for processes 4 and 5 are greater than those for processes 2 and 3.

When the solution contains no reducing agent, the number of dye molecules (or ions), N, per unit area of the electrode surface will change according to

$$dN/dt = -\eta_0 SN + kC(N_0 - N), \tag{6}$$

where η_0 is the quantum yield of the electron injection from the excited dye, S the frequency of excitation of a dye molecule (or ion), N_0 the number of the dye molecules (or ions) per unit area of the electrode before illumination, C [M] the concentration of the dye in the solution, and k the rate constant. The second term of the right hand side of Eq. 6 corresponds to the restoring rate of the oxidized dye on the electrode surface by Reaction 4.

When the concentration of the dye in the solution is very low, the second term of Eq. 6 can be neglected, and N can be written as

$$N = N_0 \exp(-\eta_0 St). \tag{7}$$

The photocurrent, assumed to be proportional to N, can be written as

$$i_{ph} = i^0_{ph} \exp(-\eta_0 St), \tag{8}$$

and, hence

$$\eta_0 = 1/\tau S. \tag{9}$$

The exponential decay of the photocurrent, as observed experimentally at the initial stage, coincides with Eq. 8.

The dependence of τ on the concentration of the dye shown in Fig. 5b can be explained as follows. When the concentration of the dye is high, the second term of Eq. 6 cannot be neglected. Therefore, Eqs. 7—9 are valid only in the range of the concentration where τ does not depend on C. Figure 5 shows that such a condition is satisfied when C is lower than 10^{-6} M.

The absorbance of the dye on the electrode can be written as

$$\log I_0/I = 1000\varepsilon N/N_A, \tag{10}$$

where ε [M^{-1} cm^{-1}] is the molar extinction coefficient of the dye, N_A the Avogadro constant, I_0 the number of the photons incident on a unit area of the dye layer on the electrode per second, and I the number of the photons transmitted through the same layer. Since the absorption of light by the dye layer is small, the equation can be approximated as

$$(I_0 - I)/I_0 = 1000(\ln 10)\varepsilon N/N_A, \tag{11}$$

and

$$I_0 - I = SN. \tag{12}$$

From these equations, S can be written as

$$S = 1000(\ln 10)\varepsilon I_0/N_A. \tag{13}$$

The relation that τ is inversely proportional to I_0, as shown in Fig. 4b, can be derived from Eqs. 9 and 13.

The quantum yield η_0 for Rose Bengal was determined to be 22% by applying Eqs. 9 and 13 to the experimentally obtained photocurrent decay curves. The quantum yield was obtained for the illumination at the peak wavelength, and the molar extinction coefficient was assumed to be the same as that at the peak of the absorption spectrum of the solution. The reflection factor of light at the surface of the electrode was estimated to be 0.7 from the comparison of the reflected light intensity with that from magnesium oxide powder. This means that seven tenths of the incident light, which passes through the dye layer toward the inside of zinc oxide sinter, is reflected and passes again through the dye layer on the surface of the electrode. Therefore, we employed the value of measured number of photons incident upon the sample multiplied by 1.7 for I_0 in Eqs. 10—13.

Effect of Halide Ions on the Dye-sensitized Photocurrent. Hauffe *et al.*[14)] found that the dye-sensitized photocurrent at a zinc oxide electrode was increased by addition of halide ions to the dye solution. The results shown in Fig. 6a indicate similar effects of the halide ions on the photocurrent. The increase in the photocurrent becomes greater in the sequence $Cl^- < Br^- < I^-$. This order is the same as that of the electron donating ability of the ions, *i.e.*, the oxidation potential increases in the reverse order.

Essentially, the visible spectra of the dye solution were not changed by addition of halide ions. Therefore, the effect of halide ions can be explained by assuming the formation of the exciplex between the excited dye and halide ions, the exciplex injecting an electron into the electrode efficiently. It is expected that the $1/\tau$ increases with the quantum yield of electron injection (Eq. 9). The result for chloride and bromide ions (Fig. 6b) is consistent with the expectation and supports the mechanism mentioned above. By addition of ioide ion, τ as well as i^0_{ph} increased. Iodide ion suppresses the deterioration of the dye by supplying an electron to the oxidized dye as described earlier. Therefore, in this case, the decrease of $1/\tau$ is attributable to the restoration of the oxidized dye by iodide ion, but not to the decrease of the quantum yield of electron injection.

Hauffe *et al.* proposed the reduced dye formation by the electron transfer from halide ions to the excited dye, the reduced dye injecting an electron into the electrode. According to their mechanism, the dye should not deteriorate, in contradiction with the experimental results that the decay is faster in the presence of chloride and bromide ions.

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